

Preparing perchlorates

Chapter 1: Introduction

Industrially, perchlorates are exclusively prepared by the electrochemical method. In the past, thermal decomposition of chlorate has been used but since this process is very inefficient it has been abandoned long ago. Chemical oxidation of chlorates is currently not very economical either, but it may become an option in the future. For the amateur Pyro, each of these methods may be used as we need not be concerned with the economy of the process as much as commercial operations do. The electrochemical method is convenient to use if you have a chlorate cell with the right anodes already, since then making perchlorates is simply a matter of operating the cell for a bit longer. If you can get chlorates in quantity for cheap, for example as a herbicide, the thermal decomposition method is an option. The method is quick, and requires no chemicals other than the chlorate starting material. Perchlorates can also be prepared by chemical oxidation of chlorates. The required chemicals are relatively expensive, but the method is quick and simple.

Chapter 2: Electrolytic preparation

Chlorates can be oxidized in an electrochemical cell to yield perchlorates. The preferred starting material for this method is sodium chlorate, since it is very soluble. Potassium chlorate is seldom used due to its low solubility, and ammonium chlorate should never be used since it leads to the formation of sensitive and explosive NCl_3 in the cell. Sodium perchlorate is conveniently converted in high yield to a number of other perchlorates (such as potassium and ammonium perchlorate) by double decomposition (metathesis) reactions. It is assumed from here on that sodium chlorate is used as starting material.

Cell construction

Electrochemical cells for perchlorate synthesis do not differ much from chlorate cells. The most important difference lies in the anode material. Not all anode materials suitable for chlorate synthesis can also be used for perchlorate synthesis. Most cell body materials used in chlorate cells may also be used in perchlorate cells. The effect of temperature and pH deviating from the optimal values is of much less importance in perchlorate cells. Finally, the voltage at which perchlorate cells operate is somewhat higher because the potential at which the conversion reactions take place is higher. The general structure of both cell types is the same: two working electrodes, and no diaphragm.

Electrode materials

Like in chlorate cells, stainless steel is a suitable cathode material. Mild steel may also be used. While copper and brass will also work, they may cause problems with copper contamination when they erode.

Anode materials for perchlorate cells should have a high oxygen over potential. What exactly that means is not further discussed here; it suffices to say that if the oxygen over potential at a certain anode material is not high enough oxygen will be evolved instead of chlorate oxidized to perchlorate. No perchlorate will be formed, and the anode material is usually attacked comparatively quickly. This holds also for chlorate cells, but the problem is less severe there since lower potentials are involved. Anode materials suitable for perchlorate synthesis are listed below. These are also described in the chlorate synthesis section but are repeated here for convenience.

Platinum: The obvious disadvantage of platinum is its high price. However, it corrodes only at a very slow rate and therefore provides an almost ideal anode material. High efficiency can be reached with platinum and processing of the electrolyte is greatly simplified due to the absence of insoluble anode erosion products.

Lead dioxide: Lead dioxide provides an economical alternative to platinum. Efficiency of lead dioxide anode based cells is usually slightly lower than that of platinum based cells, but the difference is small. Lead dioxide anodes are not easily bought and must be made. This takes some work and effort, but the anodes are cheap, fairly resistant to corrosion even at higher temperatures. More information on [lead dioxide anodes](#) of several types is given elsewhere on this homepage.

DSA: DSA stands for Dimensionally Stable Anode. This is the common term used to refer to anodes consisting of a layer of noble metal oxides (usually RuO_2 and TiO_2) coated onto a substrate, usually titanium. This type of anode is finding increased use in industrial cells because of its comparatively low cost when compared to platinum and its resistance to corrosion. The chemicals required to manufacture these anodes are expensive and difficult to handle. However, if the chemicals can be obtained and suitable equipment is available, the procedure to make the anode seems fairly straightforward and may be an option. For the preparation of these, the reader is referenced to the literature. Again, I'd be most interested in anyone's experiences with this type of anode.

Magnetite: This material has found use in industry in the past, but is rarely used nowadays due to its relatively high corrosion rate and low efficiency for perchlorate manufacture. The anodes are made by melting and casting $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ into the required anode shapes. I have little literature available on this material, so it is not further discussed here.

Preparing the electrolyte

Sodium perchlorate can be made directly from sodium chloride by electrolysis in which case no special electrolyte for the chlorate to perchlorate step has to be prepared. The preparation of a chloride electrolyte is described in the text on chlorates.

A cell can also be operated purely for the chlorate to perchlorate conversion. An electrolyte has to be prepared before each batch in this case. If the cell has been operated before, it is best to 'recycle' the old electrolyte and all the impure fractions obtained

during extraction and purification of the product. That way no product is wasted. When the cell is operated for the first time, a fresh electrolyte has to be prepared which can be done as follows.

Preparing fresh electrolyte

1. Prepare a saturated solution of sodium chlorate. Take about 60 grams of sodium chlorate for every 100 ml of solution and bring the solution to a boil. Then allow to cool to room temperature again. Sodium chlorate will crystallize as the solution cools. The solution is then filtered to obtain a clear saturated solution.

2. Optionally, 2 to 4 g/l of potassium dichromate, potassium chromate, sodium chromate or sodium dichromate may be added to improve efficiency. These compounds are suspected carcinogens, so if you choose to add any, know the hazards involved and act accordingly. If lead dioxide anodes are used, do not add potassium dichromate as it will only reduce efficiency. Instead, 2 to 4 g/l of sodium or potassium fluoride may be used. Although not carcinogenic, the fluorides are nasty compounds as well and should be handled properly.

Recycling old electrolyte

1. If the electrolyte is not clear but contains suspended particles, remove these by filtration.

2. Dissolve any impure material left over from purification steps.

3. Re-saturate the solution with sodium chlorate, following the same procedure as described in step 1 of 'preparing a fresh electrolyte'.

4. Like described in step 2 of 'preparing a fresh electrolyte' you may now add dichromates, chromates or fluorides if you choose to do so.

Operating the cell

Perchlorate cells are operated at a higher voltage than chlorate cells and temperature and pH do not need to be controlled within strict limits for optimal efficiency. Other than that, operation is much like that of chlorate cells.

Like explained in the theory section on chlorate cells, the voltage over a cell may fluctuate if the current is kept constant. In typical chlorate cells this results in a cell voltage of 3 to 4 volts, whereas in perchlorate cells the voltage is higher, 5 to 7 volts usually. The current is kept constant at an acceptable level with respect to anode erosion. A maximum current per volume as exists in chlorate cells does not exist in perchlorate cells. The current could in theory be increased indefinitely to increase the reaction rate, were it not that anode erosion increases with increasing current density (the current per unit of anode surface area). The current is therefore usually set by the surface area of the anode. As a rule of thumb maintain a current density of 200 mA/cm².

The influence of cell temperature is two-fold: anode erosion increases with increasing cell temperature and the cell voltage is reduced at higher temperatures. The former is obviously unwanted, while a lower cell voltage means energy is saved. In industry the temperature is of course chosen to get the best of both worlds, depending on what is more expensive: energy or anodes. We need not be concerned with economy as industry does so the temperature does not matter a lot. Try to keep it between 40 and 80 deg C. When using lead dioxide anodes, it is probably best to prevent the temperature from going very high. It can make the lead dioxide crack.

Finally, some water should be added from time to time to make up for what has evaporated. Try to maintain a constant electrolyte volume.

Running times

The required time to operate a cell depends on the current. The higher the current, the less time needed. In fact, the current is a measure of the reaction rate. Therefore, the amount of electricity that went through a cell is calculated by multiplying the current going through the cell (in amperes) by the time it has been flowing (in hours). The resulting number is measured in ampere-hours (abbreviated as Ah). To convert 100 grams of sodium to sodium perchlorate 50 Ah are required if the cell operates at 100% efficiency. In real life a cell will never reach 100% efficiency, and more electricity is needed.

Example: A 200 ml cell contains initially about 100 grams of sodium chlorate (the solubility of NaClO_3 in water is about 50 g/100ml at room temperature). Per 100 grams, 50 Ah are needed. So, if a cell operates at a current of 2 amperes, it would take $50/2 = 25$ hours to convert all chlorate to perchlorate in a cell operating at 100% efficiency. If the cell actually operates at 80% efficiency, $100/80 * 25 = 31.25$ hours (or 31 hours, 15 minutes) are needed.

If perchlorate is prepared by continuing to run a chlorate cell after all chloride has been consumed, the total run time is of course the sum of the time required for the chloride to chlorate conversion and the chlorate to perchlorate conversion.

Processing the electrolyte

When done, raw potassium perchlorate or ammonium perchlorate may be prepared from the electrolyte as follows:

Filtering

The first step is filtration. The electrolyte usually contains suspended solid particles. These consist of erosion products of the anodes, the cell walls, and the unsubmerged parts of the cathodes. These particles may be very small and are not always easily removed with common filtering paper. Filtering through a layer of diatomaceous earth (sold in shops for aquarium supplies) in a filter or on a piece of cloth sometimes solves the problem. However, even that will not always remove all solid impurities. A common impurity that is hard to remove is suspended iron hydroxide, originating from corrosion of (stainless)

steel cathodes. The fluffy, voluminous form of the material often gives it a white or yellowish foggy appearance. This is next to impossible to remove unless some sodium hydroxide or pool coagulant is added first. This causes the iron hydroxide particles to coagulate, making them easy to remove by filtration. Another possibility is to add hydrochloric acid to lower the pH to between 2 and 3. This will dissolve the iron hydroxide. If sodium hydroxide is then added to raise the pH to above 7 again, the iron hydroxide is precipitated in a more dense form which is easily removed by filtration, even with common filter paper.

Chromate and dichromate removal

If chromates or dichromates were used to increase the cells efficiency they should now be removed. Adding a solution of barium chloride to the electrolyte will precipitate any chromate or dichromate as the corresponding barium compounds. Add small amounts of a 10% barium chloride solution to the electrolyte. A yellow precipitate will form. If no more yellow precipitate is formed, filter to remove the barium compounds. A white (sometimes clearly crystalline) precipitate may form instead of a yellow precipitate. This is barium chlorate or perchlorate. If this happens, do not add any more barium chloride solution and filter to remove the precipitate.

Destruction of chlorate

The next step is the destruction of residual chlorate. Even when a cell is operated for many times the required running time, some chlorate is still present in the electrolyte. Since chlorates and perchlorates behave very differently in pyrotechnic compositions (see the [safety](#) page among others) chlorate contamination can be very dangerous. If the cell is not operated long enough to convert most of the chlorate to perchlorate the chlorate contamination may be very severe and it is unpractical and very inefficient to attempt to destroy it all. If this is the case I suggest this step is skipped, and the raw product is extracted. Ammonium perchlorate cannot be made this way, as it would result in the formation of the dangerously unstable explosive compound ammonium chlorate (also see the [safety](#) page). Conversion to potassium perchlorate may however be tried. This will of course afford a heavily chlorate contaminated batch of perchlorate, probably even something that can better be considered to be a chlorate/perchlorate mixture or perchlorate contaminated chlorate. This material could be used to an extremely limited extend in pyrotechnic compositions when it is treated as a chlorate, or, a better option, it can be used as a starting material for the thermal decomposition or chemical oxidation preparations of potassium perchlorate described later.

Residual chlorate is usually destroyed by the action of reducing agents. Sodium sulfite is used for this purpose in industrial setups. Iron(II)sulfate is another option, and the chemical can be bought in some gardening supply shops as it is used to supply plants with iron. A third method destroys chlorates by the action of strong acids. The cell electrolyte is acidified with hydrochloric acid to a pH of 1 to 2, and the solution is boiled. Chlorates will decompose and yield a yellow gas, chlorine dioxide. The gas will partially dissolve in the solution, imparting a bright yellow color to it. In high concentrations chlorine dioxide is dangerously explosive and sensitive but if done using proper

ventilation the small amounts evolved in this reaction are very unlikely to cause dangerous levels. The gas is however quite toxic and inhalation should be avoided at all times. Never do this step inside unless a well functioning fume hood can be used. After boiling for 15 minutes raise the pH to around 8 or 9 again using sodium hydroxide. This should afford a colorless solution. A qualitative test for chlorate should now be performed to make sure all chlorate has properly been destroyed. Such tests are described on the [product analysis](#) page.

If any other method is used to destroy residual chlorate the pH must always be adjusted afterwards to slightly above 7. Otherwise, traces of acid may be incorporated into the product in later steps which can make it very dangerous to use in pyrotechnic compositions.

Double decomposition

A discussion will have to be made at this point whether the intended product is ammonium or potassium perchlorate. Other perchlorates can be made as well but are not discussed here as they find very little use in pyrotechnics.

If residual chlorate was not destroyed the choice is simple since ammonium perchlorate is not an option. Ammonium chlorate could be formed in the process which is, as mentioned several times already, a dangerously unstable explosive compound the formation of which should at all times be avoided (even in trace amounts). If chlorate was properly destroyed, and a qualitative test indicates so, ammonium perchlorate may be prepared. **1.** If potassium perchlorate is the intended product, take 70 grams of potassium chloride for every 100 grams of sodium chlorate that was started with and dissolve this in the smallest volume of water possible. If instead ammonium perchlorate is required, take 50 grams of ammonium chloride and dissolve in the smallest volume of water possible.

2. Mix this solution of either potassium or ammonium chloride with the electrolyte. A white precipitate of the corresponding perchlorate should form.

3. Boil the solution and add small amounts of water until all the perchlorate has dissolved. Due to the low solubility of potassium perchlorate a large volume of water may be needed then. If a sufficiently large container is not available the solution may be split up in several portions that are later recombined.

4. When all has dissolved, check the pH of the solution. It should be neutral or slightly alkaline (above 7). If it is not, add some dilute sodium hydroxide solution to increase the pH to between 7 and 8. When this value is overshot, hydrochloric acid may be used to lower the pH again.

5. Allow the solution to cool slowly to room temperature. The perchlorate will crystallize during this. Cool the solution further to 0 deg C, and filter. Rinse the crystals in the filter with some ice-cold water. This raw product may be further purified as described below.

Purification

The product can be purified by recrystallization. This method is especially suitable for potassium perchlorate due to its low solubility. Little product will be lost, and the purity is greatly increased. Ammonium perchlorate suffers slightly worse losses when recrystallized, but still acceptable. The impure ammonium perchlorate should be discarded since recycling could result in NCl_3 formation in the cells. The losses occurring when potassium perchlorate is recrystallized are so slight recycling is hardly worth the effort (a liter of recrystallized solution contains only a few grams of perchlorate). Recrystallizing is done as follows:

1. Place the crude product in a pan and add 100 ml of water for every 20 g of raw potassium perchlorate, or 100 ml of water for every 50 gram of raw ammonium perchlorate. Bring this to a boil.
2. After it has boiled for a few minutes, add 10 ml amounts of water to the boiling solution in 5 minute intervals until all the product has dissolved.
3. Check the pH of the boiling solution. It should be neutral or slightly alkaline. If it is acidic, add potassium hydroxide solution until it is slightly alkaline ($\text{pH}=7\ldots 8$) again. If ammonium perchlorate is the intended product, use ammonia instead. If this is not done, traces of acid may be included in the final product making it very dangerous to use in pyrotechnic compositions.
4. Allow the solution to cool to room temperature. The purified product will crystallize.
5. Filter and rinse the crystals well with ice cold water. The filtrate should be discarded
6. The crystals may be dried in an oven at 100 deg C.

Chapter 3: Preparation by thermal decomposition of chlorate

Chlorates are thermodynamically unstable. Over time they will decompose into a mixture of chlorides and perchlorates. In essence, the chlorate will undergo a re ox reaction with itself (a so-called auto-oxidation reaction). Due to the kinetic stability of chlorates however, the process is slow at room temperature. A well known example of the same phenomenon is diamond: Diamonds are unstable at common pressures and temperatures. They turn into graphite extremely slowly. If a diamond is heated, the process is sped up. Similarly, if chlorates are heated the reaction rate is increased enough for it to be used as reaction pathway in the preparation of perchlorates. When potassium chlorate is used, the resulting perchlorate is easily separated from the chloride by recrystallization. There may be several other chlorates that this method can be used with, but potassium chlorate seems to be the most well investigated option. In any case, ammonium perchlorate cannot be prepared directly with this method due to the explosive and instable nature of

ammonium chlorate, as mentioned earlier. In the first large scale perchlorate plants this method was used to prepare potassium perchlorate. Ideally, this preparation is performed in an oven since it involves heating the chlorate for several hours. The chlorate used should be free of impurities that catalyze chlorate decomposition (such as most d-block metals). The following description assumes potassium chlorate will be used as a starting material.

1. Heat pure potassium chlorate to slightly over its melting point. A colorless clear liquid is obtained. Before heating make sure no organic material or other fuels are present in the chlorate or able to fall into the molten chlorate. This would result in a violent reaction. Do not overheat since this will decompose the chlorate, yielding chloride only.

2. Maintain this temperature for several hours. During this time the potassium chlorate will undergo the auto-oxidation reaction. Due to the higher melting point of potassium chloride and potassium perchlorate the melt will solidify slowly during this time. It becomes quite hard to judge the correct temperature as the melt solidifies, and if an oven is not used a thermometer is essential to judge the correct temperature. Too high a temperature will cause the perchlorate to decompose, a low temperature will result in incomplete conversion.

3. After the mixture has completely solidified, allow it to cool to room temperature. Test a sample of the cooled residue for chlorate, as described in the [analysis](#) page. If chlorate is present it needs to be destroyed before extraction of the perchlorate. [Destruction of chlorate](#) is described earlier in this text, in the section dealing with processing the electrolyte from the electrolytic preparation of perchlorates.

4. [Recrystallise](#) the residue, as described earlier. Two recrystallization steps are sometimes needed to separate the potassium perchlorate completely from the chloride as there is quite a lot present.

Chapter 4: Preparation by chemical oxidation

A third method to convert chlorates to perchlorates is by chemical oxidation. A sufficiently strong oxidizer added to a chlorate can oxidize a chlorate to a perchlorate. Suitable oxidizers are persulfates and lead dioxide in concentrated sulfuric acid. Hydrogen peroxide does not seem to work. I must admit my experience with this method is limited and I have not been able to obtain much literature about it. It is mentioned in literature however, and it is definitely a possible method that can be used with good results. If anyone has some experience with it, I would be most interested to hear about it. The experiments I have conducted involved sodium persulfate as the oxidizer. I will give an account of the general method I used, the ideas behind it and the results obtained with it. Anyone with comments, results, ideas, anything is very welcome to comment on it. If you wish to try this method this may be used as a starting point:

Theory

Persulfates are strong oxidizers. They are reduced according to the following half-reaction:

[REACTION]

The H^+ generated in this reaction will prevent it from taking place below a certain pH. When a base is added to neutralize the acid generated the reaction may go to completion. All persulfate may be consumed in the reaction. Persulfate being a stronger oxidizer than perchlorate may be used to convert chlorates to perchlorates according to the following half reaction:

[REACTION]

Neither persulfates, chlorates or perchlorates are destroyed at a significant rate at the temperature of boiling water, so the reaction rate may be increased by boiling a solution containing the reactants.

Oxidation of $KClO_3$ by persulfate

The general procedure I tried:

A solution of 30 g/l sodium persulfate was prepared and the pH raised to 14 by the addition of a concentrated sodium hydroxide solution. The sodium persulfate was obtained from an electronics supply store, where it was sold for etching printed circuit boards. A foggy solution was obtained, which was filtered. 5 ml of the clear solution obtained after filtering was added to a test tube. Approximately 1 gram of potassium chlorate was added to the same tube, and solution heated. The solution was boiled vigorously for 15 minutes during which time water was added occasionally to make up for what had evaporated. The solution was then allowed to cool. Upon cooling white crystals formed. These were filtered, washed with ice cold water and recrystallized. The crystal shape during recrystallization was observed and found to resemble that of potassium perchlorate best. As described in the [analysis](#) page, crystal shape is not a reliable way to determine the identity of a product however. The crystals obtained after recrystallization were tested qualitatively for chlorate with phenylanthranilic acid (as described in the [analysis](#) page). Chlorate was shown to be present. It seems most likely that the chlorate was only partially converted to perchlorate. Maybe the addition of more persulfate or allowing a longer reaction time will convert more chlorate to perchlorate. Destruction of the chlorate followed by recrystallization should afford a chlorate free product.

Chapter 5: Literature

1. Schumacher, J.C., "Perchlorates", New York, Reinhold Publishing Corp., 1960
2. Remy, H. "Treatise on Inorganic Chemistry", New York, Elsevier Publishing Co., 1956